



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 3/37, C08G 73/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/42285</b> <b>(43) International Publication Date:</b> 13 November 1997 (13.11.97)
<b>(21) International Application Number:</b> PCT/US97/06917 <b>(22) International Filing Date:</b> 25 April 1997 (25.04.97) <b>(30) Priority Data:</b> 60/016,807      3 May 1996 (03.05.96)      US <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> WATSON, Randall, Alan [US/US]; 14 Pendery Avenue, Cincinnati, OH 45215 (US). GOSSELINK, Eugene, Paul [US/US]; 3754 Susanna Drive, Cincinnati, OH 45251 (US). MANOHAR, Sanjeev, Krishnadas [US/US]; 2014B Meadowlawn Way, Fairfield, OH 45014 (US). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> COTTON SOIL RELEASE POLYMERS  <b>(57) Abstract</b>  Cotton soil release polymers comprising water soluble and/or dispersible, modified polyamines having functionalized backbone moieties and improved stability toward bleach. Also, laundry detergent compositions comprising these cotton soil release polymers.		

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## COTTON SOIL RELEASE POLYMERS

### FIELD OF THE INVENTION

The present invention relates to cotton soil release polymers comprising water soluble and/or dispersible, modified polyamines having functionalized backbone moieties and improved stability toward bleach. The present invention also relates to laundry detergent compositions comprising cotton soil release polymers and to methods for laundering cotton articles.

### BACKGROUND OF THE INVENTION

A wide variety of soil release agents for use in domestic and industrial fabric treatment processes such as laundering, fabric drying in hot air clothes dryers, and the like are known in the art. Various soil release agents have been commercialized and are currently used in detergent compositions and fabric softener/antistatic articles and compositions. Such soil release polymers typically comprise an oligomeric or polymeric ester "backbone".

Soil release polymers are generally very effective on polyester or other synthetic fabrics where the grease, oil or similar hydrophobic stains spread out and form a attached film and thereby are not easily removed in an aqueous laundering process. Many soil release polymers have a less dramatic effect on "blended" fabrics, that is on fabrics that comprise a mixture of cotton and synthetic material, and have little or no effect on cotton articles. The reason for the affinity of many soil release agents for synthetic fabric is that the backbone of a polyester soil release polymer typically comprises a mixture of terephthalate residues and ethyleneoxy or propyleneoxy polymeric units; the same or closely analogous to materials that comprise the polyester fibers of synthetic fabric. This similar structure of soil release agents and synthetic fabric produce an intrinsic affinity between these compounds.

Extensive research in this area has yielded significant improvements in the effectiveness of polyester soil release agents yielding materials with enhanced product performance and formulatability. Modifications of the polymer backbone as well as the selection of proper end-capping groups has produced a wide variety of polyester soil release polymers. For example, end-cap modifications, such as the use of sulfoaryl moieties and especially the low cost isethionate-derived end-capping units, have increased the range of solubility and adjunct ingredient compatibility of these polymers without sacrifice of soil release effectiveness. Many polyester soil release polymers can now be formulated into both liquid as well as solid (i.e., granular) detergents.

In contrast to the case of polyester soil release agents, producing an oligomeric or polymeric material that mimics the structure of cotton has not resulted in a cotton soil release polymer. Although cotton and polyester fabric are both comprised of long chain polymeric materials, they are chemically very different. Cotton is comprised of cellulose fibers that consist of anhydroglucose units joined by 1-4 linkages. These glycosidic linkages characterize the cotton cellulose as a polysaccharide whereas polyester soil release polymers are generally a combination of terephthalate and oxyethylene/oxypropylene residues. These differences in composition account for the difference in the fabric properties of cotton versus polyester fabric. Cotton is hydrophilic relative to polyester. Polyester is hydrophobic and attracts oily or greasy dirt and can easily be "dry cleaned". Importantly, the terephthalate and ethyleneoxy/propyleneoxy backbone of polyester fabric does not contain reactive sites, such as the hydroxyl moieties of cotton, that interact with stains in different manner than synthetics. Many cotton stains become "fixed" and can only be resolved by bleaching the fabric.

Until now the development of an effective cotton soil release agent for use in a laundry detergent has been elusive. Attempts by others to apply the paradigm of matching the structure of a soil release polymer with the structure of the fabric, a method successful in the polyester soil release polymer field, has nevertheless yielded marginal results when applied to cotton fabric soil release agents. The use of methylcellulose, a cotton polysaccharide with modified oligomeric units, proved to be more effective on polyesters than on cotton.

For example, U.K. 1,314,897, published April 26, 1973 teaches a hydroxypropyl methyl cellulose material for the prevention of wet-soil redeposition and improving stain release on laundered fabric. While this material appears to be somewhat effective on polyester and blended fabrics, the disclosure indicates these materials to be unsatisfactory at producing the desired results on cotton fabric.

Other attempts to produce a soil release agent for cotton fabric have usually taken the form of permanently modifying the chemical structure of the cotton fibers themselves by reacting a substrate with the polysaccharide polymer backbone. For example, U. S. Patent No. 3,897,026 issued to Kearney, discloses cellulosic textile materials having improved soil release and stain resistance properties obtained by reaction of an ethylene-maleic anhydride co-polymer with the hydroxyl moieties of the cotton polymers. One perceived drawback of this method is the desirable hydrophilic properties of the cotton fabric are substantially modified by this process.

Non-permanent soil release treatments or finishes have also been previously attempted. U.S. Patent No. 3,912,681 issued to Dickson teaches a composition for

applying a non-permanent soil release finish comprising a polycarboxylate polymer to a cotton fabric. However, this material must be applied at a pH less than 3, a process not suitable for consumer use nor compatible with laundry detergents which typically have a pH greater than 7.5.

U.S. Patent No. 3,948,838 issued to Hinton, *et alia* describes high molecular weight (500,000 to 1,500,000) polyacrylic polymers for soil release. These materials are used preferably with other fabric treatments, for example, durable press textile reactants such as formaldehyde. This process is also not readily applicable for use by consumers in a typical washing machine.

U.S. Patent 4,559,056 issued to Leigh, *et alia* discloses a process for treating cotton or synthetic fabrics with a composition comprising an organopolysiloxane elastomer, an organosiloxaneoxyalkylene copolymer crosslinking agent and a siloxane curing catalyst. Organosilicone oligomers are well known by those skilled in the art as suds suppressors

Other soil release agents not comprising terephthalate and mixtures of polyoxy ethylene/propylene are vinyl caprolactam resins as disclosed by Rupert, *et alia* in U.S. Patent Nos. 4,579,681 and 4,614,519. These disclosed vinyl caprolactam materials have their effectiveness limited to polyester fabrics, blends of cotton and polyester, and cotton fabrics rendered hydrophobic by finishing agents.

Examples of alkoxylated polyamines and quaternized alkoxylated polyamines are disclosed in European Patent Application 206,513 as being suitable for use as soil dispersants, however their possible use as a cotton soil release agent is not disclosed. In addition, these materials do not comprise N-oxides, a key modification made to the polyamines of the present invention and a component of the increased bleach stability exhibited by the presently disclosed compounds.

It has now been surprisingly discovered that effective soil release agents for cotton articles can be prepared from certain modified polyamines. This unexpected result has yielded compositions that are effective at providing the soil release benefits once available to only synthetic and synthetic-cotton blended fabric.

The present invention provides for soil release agents that are effective on articles that comprise cotton as well as articles that comprise blends of cotton and certain synthetic fibers. The present invention also provides for laundry detergent compositions that are solid or liquid. The solid laundry detergents may be in the form of granules, flakes, pastes, gels or laundry bars. The liquid detergents can have a wide range of viscosity and may include heavy concentrates, pourable "ready" detergents, or light duty fabric pre-treatments.

The compounds of the present invention are compatible with other laundry detergent additives and adjuncts and when formulated with polyester soil release agents, now provide soil release on all fabrics.

### BACKGROUND ART

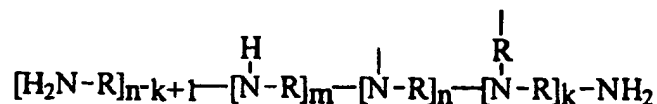
In addition to the above cited art, the following disclose various soil release polymers or modified polyamines; U.S. Patent 4,548,744, Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1, 1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado, et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May 16, 1995; U.S. Patent 4,235,735, Marco, et al., issued November 25, 1980; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent 1,498,520, published January 18, 1978; WO 95/32272, published November 30, 1995; German Patent DE 28 29 022, issued January 10, 1980; Japanese Kokai JP 06313271, published April 27, 1994.

### SUMMARY OF THE INVENTION

The present invention relates to water soluble or dispersible, modified polyamines which provide cotton soil release benefits, comprising a polyamine backbone corresponding to the formula:

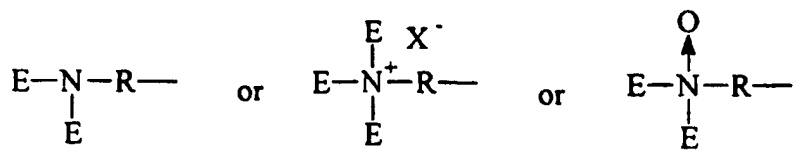


having a modified polyamine formula  $V_{(n+1)}W_mY_nZ$  or a polyamine backbone corresponding to the formula:

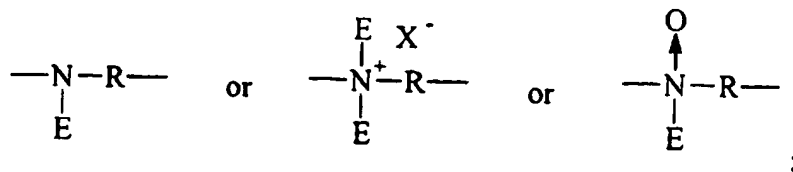


having a modified polyamine formula  $V_{(n-k+1)}W_mY_nY'_kZ$ , wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

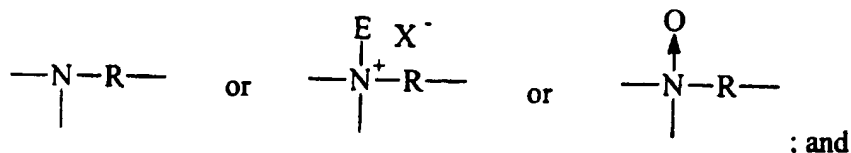
- i) V units are terminal units having the formula:



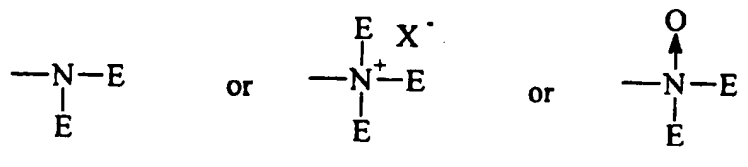
ii) W units are backbone units having the formula:



iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C<sub>1</sub>-C<sub>12</sub> alkylene, -(R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>O-(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-, and mixtures thereof; provided that when R comprises C<sub>1</sub>-C<sub>12</sub> alkylene, R also comprises at least one -(R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>O-(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, or -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-, unit; R<sup>1</sup> is C<sub>2</sub>-C<sub>6</sub> alkylene and mixtures thereof; R<sup>2</sup> is hydrogen, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof; R<sup>3</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxy-alkylene, C<sub>8</sub>-C<sub>12</sub> dialkyl-arylene, -C(O)-, -C(O)NHR<sup>5</sup>NH-C(O)-, -R<sup>1</sup>(OR<sup>1</sup>)-, -C(O)(R<sup>4</sup>)<sub>r</sub>C(O)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>O-CH<sub>2</sub>CH(OH)CH<sub>2</sub>-, and mixtures thereof; R<sup>4</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>4</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, and mixtures thereof; R<sup>5</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene or C<sub>6</sub>-C<sub>12</sub> arylene; E units are selected from the group consisting of hydrogen, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>CH(SO<sub>3</sub>M)-CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>CH(SO<sub>2</sub>M)-CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -PO<sub>3</sub>M, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; k has the value from 0 to about 20; m has

the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

The present invention also relates to laundry detergent compositions that provide a non-cotton fabric soil release benefit together with a cotton soil release benefit said compositions comprising an effective amount of non-cotton as well as cotton soil polymers. What is meant by an effective amount herein is that amount of cotton soil release polymer which is sufficient to enhance the release of oils, dirt, soil, clay and other deposits from cotton and cotton blended fabric. Typically, the laundry compositions of the present invention employ at least 0.01 % by weight of one or more of the cotton soil release polymers.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ( $^{\circ}$  C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

The water soluble or dispersible, modified polyamines of the present invention provide cotton soil release benefits. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

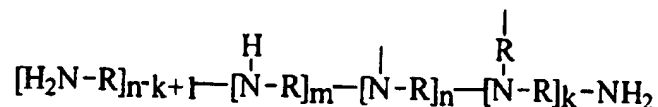
For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution must be accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the cotton soil release agents of the present invention have the general formula:



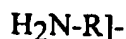


said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones comprising the cotton soil release agents of the present invention have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

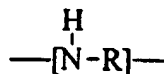


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

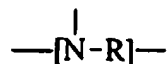
In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified, but according to the present invention some backbone units must be modified. These

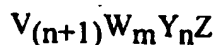
unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

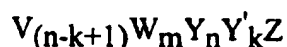


is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

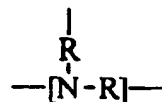
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



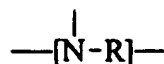
for linear or branched polyamine cotton soil release polymers and by the general formula



for cyclic polyamine cotton soil release polymers. For the case of polyamines comprising rings, a Y' unit of the formula



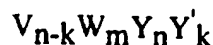
serves as a branch point for a backbone or branch ring. Except in the cases wherein the backbone comprises a ring, then for every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

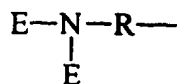


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred. As further defined herein below, when the ratio of m : n is approximately 2 : 1 m is preferably less than 200.

Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

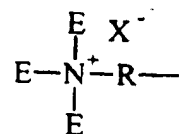
Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- a) simple substituted units having the structure:



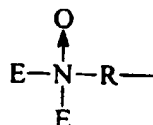
- b) quaternized units having the structure:

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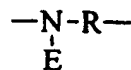
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

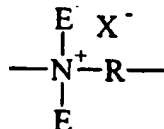


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

a) simple substituted units having the structure:

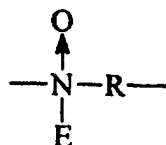


b) quaternized units having the structure:



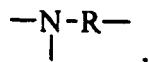
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



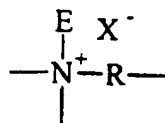
Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

a) unmodified units having the structure:



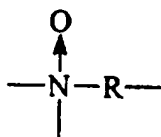
b) quaternized units having the structure:

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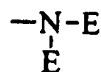
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

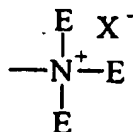


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

a) simple substituted units having the structure:

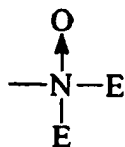


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH<sub>2</sub>CH<sub>2</sub>)HN-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH<sub>2</sub>. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic

polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefor E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C<sub>2</sub>-C<sub>12</sub> alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise  $-(R^1O)_xR^3(OR^1)_x-$ ,  $-\text{CH}_2\text{CH}(OR^2)\text{CH}_2\text{O}_z(R^1O)_yR^1O-$ ,  $(\text{CH}_2\text{CH}(OR^2)\text{CH}_2)_w-$ ,  $-\text{CH}_2\text{CH}(OR^2)\text{CH}_2-$ , and mixtures thereof; preferred "oxy" R units are  $-\text{CH}_2\text{CH}(OR^2)\text{CH}_2-$ ,  $-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(R^1O)_yR^1O-$ ,  $\text{O}(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2)_w-$ , and mixtures thereof. The backbone R units of the present invention must comprise at least one  $-\text{CH}_2\text{CH}(OR^2)\text{CH}_2-$ ,  $-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(R^1O)_yR^1O(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2)_w-$ ,  $-\text{CH}_2\text{CH}(OR^2)\text{CH}_2-$ , or mixtures thereof.

R<sup>1</sup> units are C<sub>2</sub>-C<sub>6</sub> alkylene, and mixtures thereof, preferably ethylene.

R<sup>2</sup> is hydrogen, and  $-(R^1O)_xB$ , preferably hydrogen.

R<sup>3</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene,  $-\text{C}(\text{O})-$ ,  $-\text{C}(\text{O})\text{NHR}^6\text{NHC}(\text{O})-$ ,  $-\text{C}(\text{O})(\text{R}^4)_r\text{C}(\text{O})-$ ,  $-\text{R}^1(\text{OR}^1)-$ ,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{R}^1\text{O})_y\text{R}^1\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$ ,  $-\text{C}(\text{O})(\text{R}^4)_r\text{C}(\text{O})-$ ,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ , R<sup>3</sup> is preferably ethylene,  $-\text{C}(\text{O})-$ ,  $-\text{C}(\text{O})\text{NHR}^5\text{NHC}(\text{O})-$ ,  $-\text{R}^1(\text{OR}^1)-$ ,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{R}^1\text{O})_y\text{R}^1\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$ , more preferably  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ .

R<sup>4</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>4</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, preferably C<sub>1</sub>-C<sub>10</sub> alkylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, more preferably C<sub>2</sub>-C<sub>8</sub> alkylene; most preferably ethylene or butylene.

R<sup>5</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene or C<sub>6</sub>-C<sub>12</sub> arylene

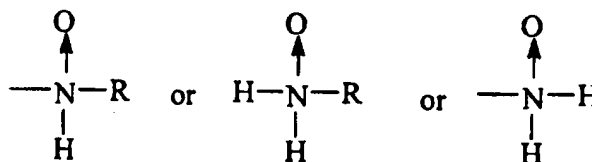
The preferred "oxy" R units are further defined in terms of the R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> units. Preferred "oxy" R units comprise the preferred R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> units. The preferred cotton soil release agents of the present invention comprise at least 50% R<sup>1</sup> units that are ethylene. Preferred R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

- i) Substituting more preferred R<sup>3</sup> into  $-(\text{CH}_2\text{CH}_2\text{O})_x\text{R}^3(\text{OCH}_2\text{CH}_2)_x-$  yields  $-(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CHOHCH}_2(\text{OCH}_2\text{CH}_2)_x-$ .

- ii) Substituting preferred  $R^1$  and  $R^2$  into  $-(CH_2CH(OR^2)CH_2O)_z-$   $(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$  yields  $-(CH_2CH(OH)CH_2O)_z-$   $(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$ .
- iii) Substituting preferred  $R^2$  into  $-CH_2CH(OR^2)CH_2-$  yields  $-CH_2CH(OH)CH_2-$ .

E units are selected from the group consisting of  $-(CH_2)_pCO_2M$ ,  $-(CH_2)_qSO_3M$ ,  $-CH(CH_2CO_2M)CO_2M$ ,  $-(CH_2)_pPO_3M$ ,  $-(R^1O)_xB$ , preferably  $-(R^1O)_xB$ ,  $(CH_2)_pCO_2M$ ,  $-(CH_2)_qSO_3M$ ,  $CH(CH_2CO_2M)CO_2M$ , more preferably  $-(R^1O)_xB$ . When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



B is hydrogen,  $-(CH_2)_pCO_2M$ ,  $-(CH_2)_qSO_3M$ ,  $-(CH_2)_qCH(SO_3M)-CH_2SO_3M$ ,  $-(CH_2)_qCH(SO_2M)CH_2SO_3M$ ,  $-(CH_2)_pPO_3M$ ,  $-PO_3M$ , preferably hydrogen,  $-(CH_2)_qSO_3M$ ,  $-(CH_2)_qCH(SO_3M)CH_2SO_3M$ ,  $-(CH_2)_qCH(SO_2M)-CH_2SO_3M$ , more preferably hydrogen or  $-(CH_2)_qSO_3M$ .

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies  $-(CH_2)_pCO_2M$ , and  $-(CH_2)_qSO_3M$ , thereby resulting in  $-(CH_2)_pCO_2Na$ , and  $-(CH_2)_qSO_3Na$  moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a  $-(CH_2)_pPO_3M$  moiety substituted with sodium atoms has the formula  $-(CH_2)_pPO_3Na_2$ . Divalent cations such as calcium ( $Ca^{2+}$ ) or magnesium ( $Mg^{2+}$ ) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine ( $Cl^-$ ), bromine ( $Br^-$ ) and iodine

(I<sup>-</sup>) or X can be any negatively charged radical such as sulfate (SO<sub>4</sub><sup>2-</sup>), methosulfate (CH<sub>3</sub>OSO<sub>3</sub><sup>-</sup>), and methanesulfonate (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>).

The formula indices have the following values: p has the value from 1 to 6; q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; k has the value from 0 to about 20; m has the value from 4 to about 400; n has the value from 0 to about 200; preferably m + n has the value of at least 5.

The preferred cotton soil release agents of the present invention comprise polyamine backbones wherein less than about 100% of the R groups comprise "oxy" R units, preferably less than about 50% , more preferably less than 30%, most preferably less than about 20% of the R units comprise "oxy" R units.

The preferred cotton soil release agents of the present invention comprise polyamine backbones wherein less than 50% of the "hydrocarbyl" R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C<sub>2</sub>-C<sub>12</sub> alkylene, preferred is C<sub>2</sub>-C<sub>3</sub> alkylene, most preferred is ethylene.

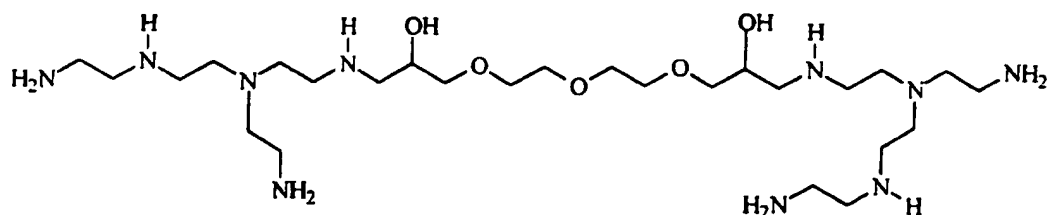
The cotton soil release agents of the present invention comprise modified non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention.

For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the cotton soil release agents of the present invention.

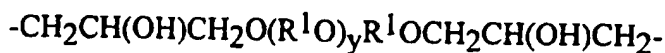
An example of a polyamine backbone according to the present invention prior to modification has the formula



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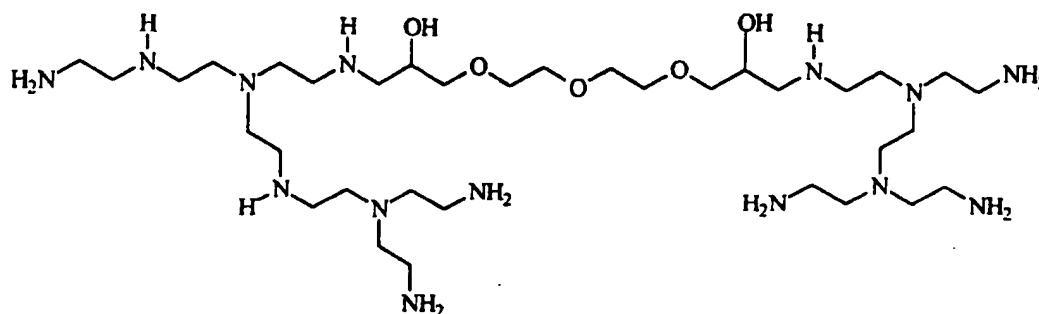


wherein 8 R units comprise ethylene units and 1 R unit comprises a

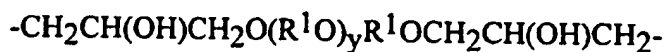


moiety wherein  $\text{R}^1$  is ethylene and  $y$  is equal to 1.

A further example of a polyamine backbone prior to modification that is suitable for use as a cotton soil release agent according to the present invention has the formula



wherein 12 R units comprise ethylene units and 1 R unit comprises a



moiety wherein  $\text{R}^1$  is ethylene and  $y$  is equal to 1. Structures similar to these two examples given above are for the purposes of the present invention commonly referred to as "blocks". Typically several blocks are combined to form the final backbone prior to modification.

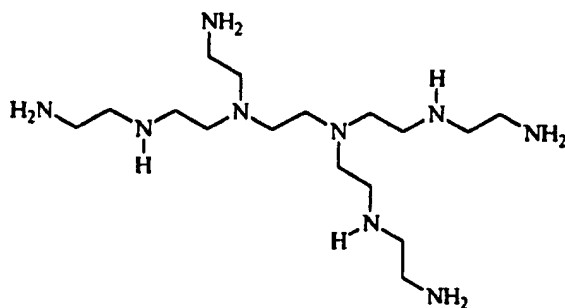
As in the examples above, polyethyleneimines (PEI's) and polyethyleneamines (PEA's) of low molecular weight, typically below 600 daltons, are linked together using the "oxy" R units which serve as convenient coupling agents. Depending on the desired properties of the final cotton soil release agent (e.g., solubility, fabric substantivity) a lesser or greater degree of "oxy" R units will comprise the polyamine backbone.

It is more convenient for nitrogen modification to occur after complete assembly of the polyamine backbone. However the formulator may wish to have a polymer backbone with a high degree of unmodified nitrogen atoms. This can be accomplished by pre-modifying some or all of the polyalkyleneimine or

polyalkyleneamine "hydrocarbyl" portion of the backbone prior to linking via "oxy" R units.

An example of a procedure that allows for a mixture of modified and unmodified blocks in the cotton soil release polymer, comprises the steps of

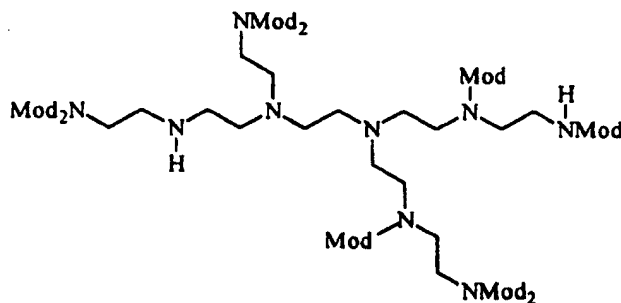
- i) modifying a polyethyleneimine having, for example, the formula:



wherein the modification is

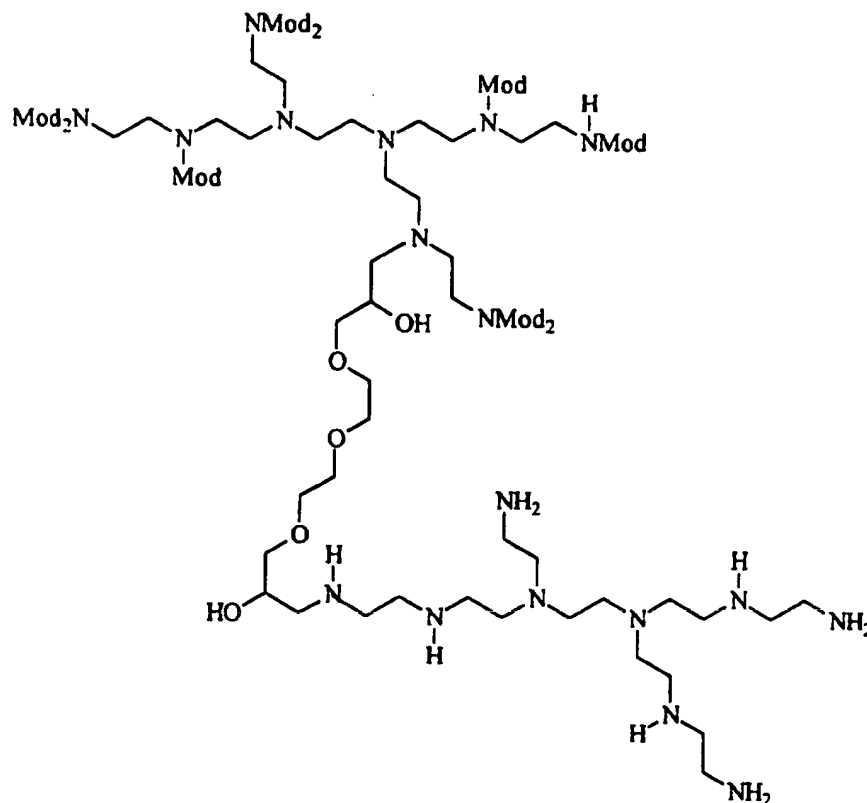
- a) substitution of the -NH hydrogen atom by an E unit;
- b) quaternization;
- c) oxidation to the N-oxide; or
- d) mixtures thereof;

resulting in an example modified polyethyleneimine having the formula:



wherein Mod represents one or more modifications according to the present invention;

- ii) the modified polyethyleneimine is coupled with a second molecule of the original unmodified polyethyleneimine through an  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{R}^1\text{O})_y\text{R}^1\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$  moiety wherein  $\text{R}^1$  is ethylene and  $y$  is equal to 1, to form a polyamine cotton soil release agent having the formula:



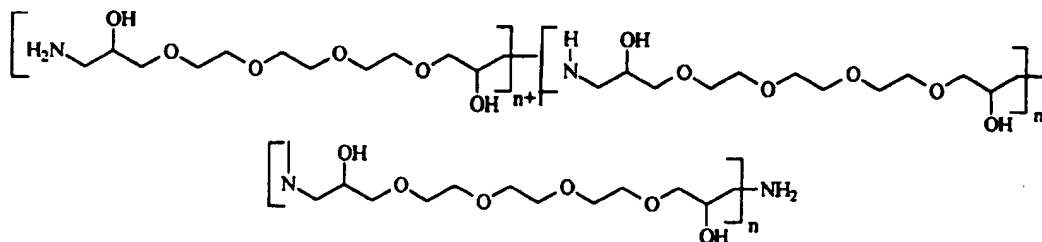
Once this process is completed, the above unit may be used "as is" or may be further coupled to one or more modified or un-modified blocks.

The preferred "blocks" of polyamines having "hydrocarbyl" R units that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's) units. An example of a polyalkyleneamine (PAA) is tetrabutylene-pentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

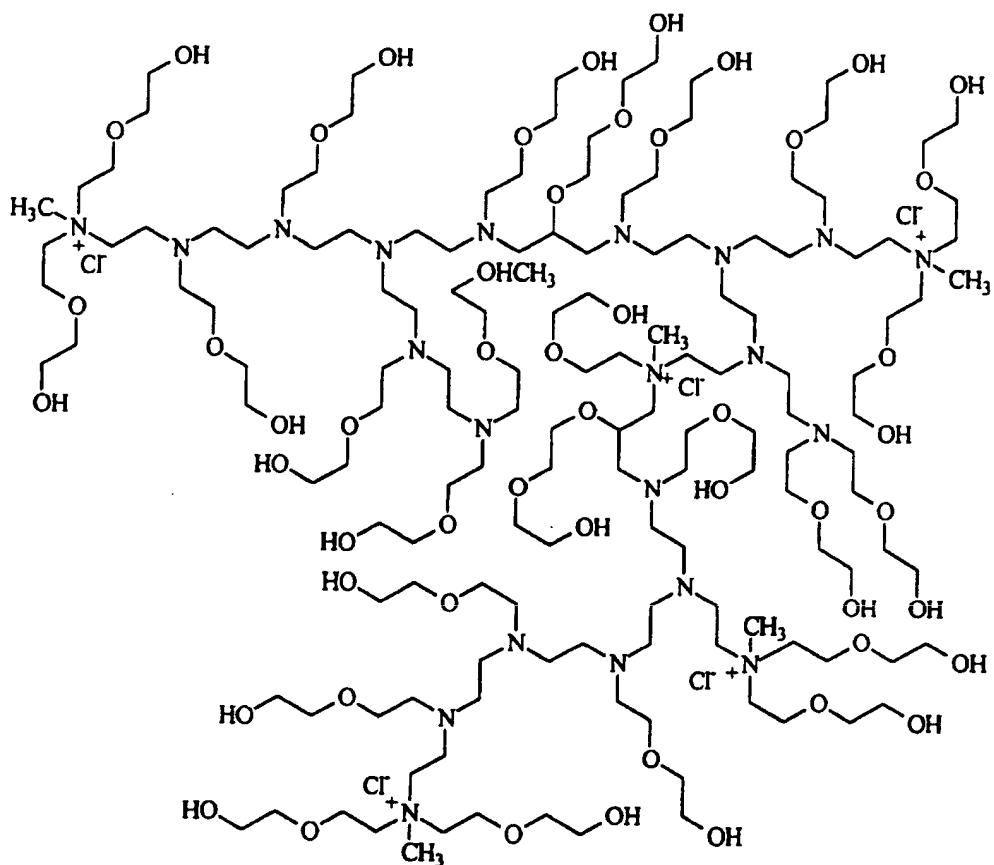
The PEI blocks which comprise the preferred backbones of the polyamines of the present invention can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific

methods for preparing PEI's are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951 (all herein incorporated by reference). In addition to the linear and branched PEI's, the present invention also includes the cyclic amines that are typically formed as artifacts of synthesis. The presence of these materials may be increased or decreased depending on the conditions chosen by the formulator.

However, polyamine backbones of the present invention may comprise 100% "oxy" moieties, for example, a polyamine backbone prior to modification comprising  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{R}^1\text{O})_y\text{R}^1\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$  R units wherein  $\text{R}^1$  is ethylene and y is equal to 1, has the formula



An example of a soil release agent according to the present invention has the formula:



wherein R units are ethylene and  $-\text{CH}_2\text{CH}[(\text{CH}_2\text{CH}_2\text{O})_2\text{H}]\text{CH}_2-$  and the E units are  $-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$  and  $-\text{CH}_3$ .

The polyamines of the present invention may develop undesirable off-colors due to impurities present as artifacts of their preparation or produced during processing or handling of the polyamines. In the case where the presence of color is unacceptable in the final formulation, the processor or formulator may apply one or more known procedures for "de-colorizing" the polyamines of the present invention. This de-colorizing may be accomplished at any stage in the processing of the polyamines disclosed herein, provided said processing does not limit or diminish the effectiveness of the final heavy metal ion control agents.

Treatment with activated charcoal in the presence of a suitable solvent is a common procedure for de-colorizing organic materials and may be applied to the polyamines of the present invention. Contact with silicates or diatomaceous earth are additional de-colorizing measures. Treatment with bleaching agents (e.g., hypochlorites or peracids) also serves as a suitable method for de-colorizing the chelants of the present invention provided that once de-colorizing with a bleaching agent is accomplished, the formulator insures that little or no active bleaching agent is carried throughout to the formulation, as described in detail hereinafter.

The present invention also relates to laundry detergent compositions comprising:

- a) at least 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine cotton soil release agent of the present invention; and
- b) the balance carrier and adjunct ingredients.

Preferably the laundry detergent compositions of the present invention comprise:

- a) at least 0.01% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, and ampholytic surfactants, and mixtures thereof;
- b) from about 0.1 to about 10% by weight, a modified polyamine cotton soil release polymer according to the present invention; and
- c) the balance carrier and adjunct ingredients.

More preferably the laundry detergent compositions of the present invention comprise:

- a) at least 0.01% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, and ampholytic surfactants, and mixtures thereof;
- b) from about 0.01 to about 10% by weight, of a soil release polymer having effective soil release on non-cotton fabric;
- c) optionally from about 0.05 to about 30% by weight, of a bleach;
- d) from about 0.1 to about 10% by weight, a modified polyamine cotton soil release polymer according to the present invention; and
- e) the balance carrier and adjunct ingredients.

In the above more preferred embodiment what is meant by the term "effective soil release on non-cotton fabric" is that amount of polyester or cotton-polyester effective soil release agent which provides soil release benefits, typically at least from about 0.01% to about 10% by weight, is effective. Suitable non-cotton soil release agents are further described herein below.

The laundry detergent composition may be in any suitable form, for example, high density liquids, light liquids or other pourable forms in addition to granules or laundry bars. The cotton soil release polymers of the present invention can be formulated into any deterative matrix chosen by the formulator.

The laundry detergent compositions according to the present invention comprise adjunct ingredients and carriers, said adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters,

bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, enzyme activators, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, and mixtures thereof, however this list is not meant to be exhaustive or to exclude any suitable material used by the formulator.

#### Deterstive surfactants

The deterstive surfactants suitable for use in the present invention are cationic, anionic, nonionic, ampholytic, zwitterionic, and mixtures thereof, further described herein below. The laundry detergent composition may be in any suitable form, for example, high density liquids, light liquids or other pourable forms in addition to granules or laundry bars. The cotton soil release polymers of the present invention can be formulated into any deterstive matrix chosen by the formulator.

The laundry detergent compositions according to the present invention comprise at least about 0.01%, preferably at least about 0.1%, more preferably at least about 1% by weight, of a deterstive surfactant. Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C<sub>10</sub>-C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>10</sub>-C<sub>18</sub> secondary (2,3) alkyl sulfates of the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>(CHOSO<sub>3</sub><sup>-</sup>M<sup>+</sup>)CH<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>(CHOSO<sub>3</sub><sup>-</sup>M<sup>+</sup>)CH<sub>2</sub>CH<sub>3</sub> where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AE<sub>x</sub>S"; especially EO 1-7 ethoxy sulfates), C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-18 glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like, can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used. Mixtures of anionic and

nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

#### Non-cotton Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic species, see U.S. 4,956,447, issued September 11, 1990 to Gosselink, et al., as well as noncharged monomer units, and their structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by



transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyoxyethylene or polyoxypropylene terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C<sub>1</sub>-C<sub>4</sub> alkyl celluloses and C<sub>4</sub> hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C<sub>1</sub>-C<sub>6</sub> vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 80-90% by weight of polyoxyethylene terephthalate derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

Another preferred SRA is an oligomer having empirical formula  $(CAP)_2(EG/PG)_5(T)_5(SIP)_1$  which comprises terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propyleneoxy (EG/PG) units and which is preferably terminated with end-caps (CAP), preferably modified isethionates, as in an oligomer comprising one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a defined ratio, preferably about 0.5:1 to about 10:1, and two end-cap units derived from sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said SRA preferably further comprises from 0.5% to 20%, by weight of the oligomer, of a crystallinity-reducing stabilizer, for example an anionic surfactant such as linear sodium dodecylbenzenesulfonate or a member selected from xylene-, cumene-, and toluene- sulfonates or mixtures thereof, these stabilizers or modifiers being introduced into the synthesis vessel, all as taught in U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na-2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl-5-sulfoisophthalate, EG and PG.

Yet another group of preferred SRA's are oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred are esters of the empirical formula:



wherein CAP, EG/PG, PEG, T and SIP are as defined hereinabove, (DEG) represents di(oxyethylene)oxy units, (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units, (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, x is from about 1 to about 12, y' is from about 0.5 to about 25, y'' is from 0 to about 12, y''' is from 0 to about 10, y'+y''+y''' totals from about 0.5 to about 25, z is from about 1.5 to about 25, z' is from 0 to about 12; z + z' totals from about 1.5 to about 25, q is from about 0.05 to about 12; m is from about 0.01 to about 10, and x, y', y'', y''', z, z', q and m represent the average number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from about 500 to about 5,000.

Preferred SEG and CAP monomers for the above esters include Na-2-(2,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2-hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred SRA esters in this class include the product of transesterifying and oligomerizing sodium 2-{2-(2-hydroxyethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)ethoxy}-ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is  $(\text{Na}+\text{O}_3\text{S}[\text{CH}_2\text{CH}_2\text{O}]3.5)-$  and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF, made by grafting acrylic monomers onto sulfonated polyesters. These SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie. Still other classes include: (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate onto proteins such as caseins, see EP 457,205 A to BASF (1991); and (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al., DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989 and 4,525,524.

#### Bleaching Compounds - Bleaching Agents and Bleach Activators

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach

activators. When present, bleaching agents will be at levels of from about 0.05% to about 30%, more preferably from about 1% to about 30%, most preferably from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

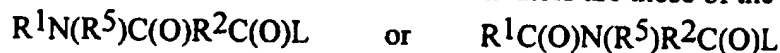
A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in

aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

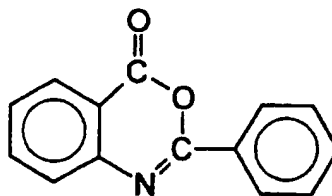
Highly preferred amido-derived bleach activators are those of the formulae:



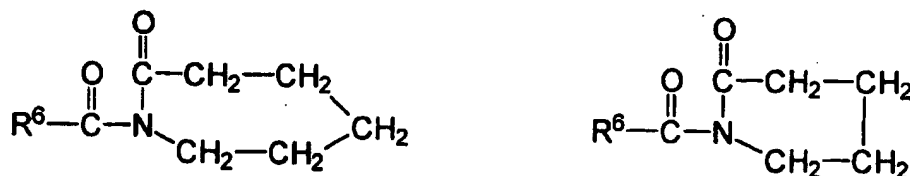
wherein R<sup>1</sup> is an alkyl group containing from about 6 to about 12 carbon atoms, R<sup>2</sup> is an alkylene containing from 1 to about 6 carbon atoms, R<sup>5</sup> is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R<sup>6</sup> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam,

octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$ ,  $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_3(\text{OCH}_3)_3(\text{PF}_6)$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the  $\text{C}_{10}$ - $\text{C}_{16}$  alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The  $\text{C}_{10}$ - $\text{C}_{14}$  monoethanol and diethanol amides illustrate a

typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ , and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of  $\text{C}_{13-15}$  ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerin, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Granular laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

#### Enzymes

Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from



International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Amylases suitable herein, include, for example,  $\alpha$ -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at

common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus*  $\alpha$ -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such

formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

#### Enzyme Stabilizing System

Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric

acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions, may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed

with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

#### Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

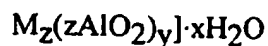
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- $\text{Na}_2\text{SiO}_5$  morphology form of layered silicate. It can be prepared by

methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{SiO}_5$  (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

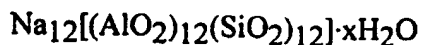
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ( $x = 0 - 10$ ) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of

carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.



Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

#### Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein. Also suitable for use as a chelant is methylglycine di-acetic acid (MGDA).

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et

al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

#### Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

#### Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower

molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

#### Brightener

Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-stryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(stryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-stryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

#### Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as

described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein

the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of  $(\text{CH}_3)_3\text{SiO}_{1/2}$  units of  $\text{SiO}_2$  units in a ratio of from  $(\text{CH}_3)_3\text{SiO}_{1/2}$  units and to  $\text{SiO}_2$  units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature

of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C<sub>6</sub>-C<sub>16</sub> alkyl alcohols having a C<sub>1</sub>-C<sub>16</sub> chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

#### Fabric Softeners

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

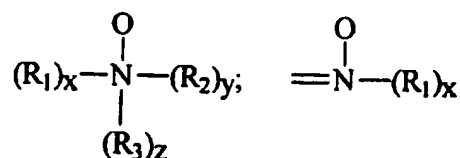
Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula:  $R-A_x-P$ ; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can



form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a  $\text{pK}_a < 10$ , preferably  $\text{pK}_a < 7$ , more preferred  $\text{pK}_a < 6$ .

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

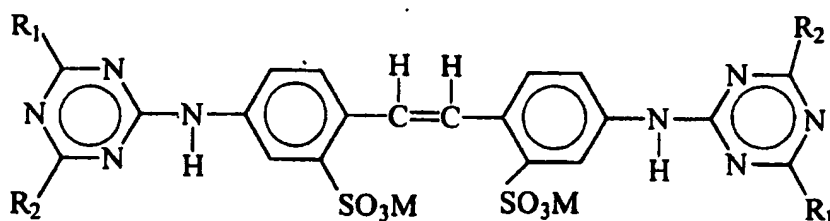
Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al.,

Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein  $R_1$  is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl;  $R_2$  is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R<sub>1</sub> is anilino, R<sub>2</sub> is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R<sub>1</sub> is anilino, R<sub>2</sub> is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

The modified polyamines of the present invention useful as cotton soil release agents are suitably prepared by the following methods.

#### EXAMPLE 1

##### Reaction of tetraethylenepentamine with epichlorohydrin

To a 250ml three-neck round bottom flask equipped with a magnetic stirring bar, condenser, addition funnel, thermometer, and temperature-controlling device (Thermowatch, I<sup>2</sup>R) is added tetraethylenepentamine (25.0g, 0.132 mol) and

methanol (60g, 1.87 mol). This solution is heated to reflux under argon, and epichlorohydrin (24.9g, 0.269 mol) is weighed into the addition funnel and added dropwise. After about half of the epichlorohydrin is added, the solution begins to look hazy. Addition is stopped, and the solution is heated at reflux overnight. A  $^{13}\text{C}$ -NMR ( $\text{D}_2\text{O}$ ) is taken, which shows the absence of an epichlorohydrin peak at  $\sim 45\text{ppm}$ . The remaining epichlorohydrin is added, and the solution is heated at reflux overnight. A  $^{13}\text{C}$ -NMR ( $\text{D}_2\text{O}$ ) again shows no remaining epichlorohydrin. The methanol is removed on a Kugelrohr apparatus (Aldrich) at about  $80^\circ\text{C}$  to afford 40.2g of sticky yellow solid. The material is almost all soluble in water but on standing separates a small amount of gelatinous material. Size exclusion chromatography indicates that the material has a broad molecular weight distribution. Prior to ethoxylation, it is rigorously dried under vacuum at  $130^\circ\text{C}$ .

### EXAMPLE 2

#### Preparation of 6 unit hexaethyleneheptamine backbone linked by 2-hydroxypropyl units.

To a 1000 mL round bottom flask equipped with an overhead stirrer, temperature control unit (Thermowatch, I<sup>2</sup>R) and argon inlet tube is charged hexaethyleneheptamine (27.5 gm, 0.10 mole) and methanol (500 mL). Epichlorohydrin (77.1 gm, 0.083 mole) is added dropwise with sufficient stirring. The reaction solution is refluxed and the reaction completion is determined by the complete disappearance of the oxirane ring carbon  $^{13}\text{C}$  NMR resonance. Several milligrams of tetrabutylammonium hydroxide phase transfer catalyst is added followed by KOH (4.0 gm, 0.10 mole) as a 40% aqueous solution. The thickened two phase solution is diluted with water (100 mL) and the phases separated. The reaction is allowed to dry over  $\text{Na}_2\text{SO}_4$ , the solvent is removed by rotary evaporation and the coupled heptamine backbone is used without further purification.\* Prior to further use, it is rigorously dried under vacuum at  $130^\circ\text{C}$ .  
\* If necessary, the number of heptamine blocks that comprise the backbone can be determined by NMR analysis of the number of primary amine moieties present.

### EXAMPLE 3

#### Mono-ethoxylation of 2-hydroxypropyl-linked-tetraethylenepentamine backbone

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A  $\sim 20$  lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 1500 g portion of 2-hydroxypropyl-linked-tetraethylenepentamine backbone (comprising a mixture of tetraethylenepentamine units linked with 2-hydroxypropyl units) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 1800 grams of ethylene oxide has been charged to the autoclave, the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. This mono-ethoxylated mixture of tetraethylenepentamine units connected by 2-hydroxypropyl units is suitable for use as is as a non-cotton soil release agent according to the present invention or may be further modified.

#### EXAMPLE 4

##### General procedure for Ethoxylation of 2-hydroxypropyl-linked-tetraethylenepentamine backbone

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 1170 g portion of 2-hydroxypropyl-linked-tetraethylenepentamine backbone (comprising a mixture of tetraethylenepentamine units linked with 2-hydroxypropyl units having an average of five tetraethylenepentamine blocks linked by 2-propyl units) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents

are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 1800 grams of ethylene oxide has been charged to the autoclave, the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing sufficient sodium methoxide in methanol solution to achieve a 10% catalyst loading based upon the total number of nitrogen and hydroxy functions (in this example, 27 moles of -NH's and 4 moles of -OH's are present on average and therefore 3.1 moles of sodium methoxide is used.). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide (8360 gm) is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of the theoretical amount of ethylene oxide to form 6 additional ethyleneoxy units per -NH unit and 7 ethyleneoxy units per -OH unit is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding methanesulfonic acid until neutral by pH paper. The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product. This material may be used as is as a suitable cotton soil release agent of the present invention or may be further modified.

#### EXAMPLE 5

##### Ethoxylation of 2-hydroxypropyl-linked-hexaethyleneheptamine backbone

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 2100 g portion of 2-hydroxypropyl-linked-hexaethyleneheptamine backbone (comprises 6 equivalents of hexaethyleneheptamine linked with 5 equivalents of 2-hydroxypropyl units equating to 43 moles of nitrogen functions per mole and 5 hydroxy functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 1800 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is

increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 420 g of a 25% sodium methoxide in methanol solution (1.94 moles, to achieve a 10% catalyst loading based upon the total number of nitrogen and hydroxy functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 5100 g of ethylene oxide (resulting in a total of approximately 7 moles of ethylene oxide per mole of substitutable sights, 43 nitrogen functions and 5 hydroxy functions) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.94 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product. This material may be used as is as a



suitable cotton soil release agent of the present invention or may be further modified.

#### EXAMPLE 6

##### Quaternization of (tetraethylenepentamine)<sub>5</sub>-(2-hydroxypropyl)<sub>4</sub> E<sub>7</sub>

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added (108 gm, 0.01 mole) of the polyamine comprising an average of 5 tetraethylene-pentamine blocks wherein each block is connected by a 2-hydroxypropyl unit (prepared as in Example 1) wherein each substitutable backbone site (27 -NH sites + 4 -OH sites) is ethoxylated to an average of 7 ethyleneoxy units per site, the ethoxylated material having an average molecular weight of 10,767 and acetonitrile (120 g). This material comprises an average 0.25 moles of quaternizable nitrogen atoms per mole of polymer. Dimethyl sulfate (14.1g, 0.112 mol) is added in one portion to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is removed by rotary evaporation at about 60°C, followed by further stripping of solvent using a Kugelrohr apparatus at approximately 80°C to afford 113 g of the desired partially quaternized material as a dark brown viscous liquid. The <sup>13</sup>C-NMR (D<sub>2</sub>O) spectrum obtained on a sample of the reaction product indicates the absence of a carbon resonance at ~58ppm corresponding to dimethyl sulfate. The <sup>1</sup>H-NMR (D<sub>2</sub>O) spectrum shows a partial shifting of the resonance at about 2.5 ppm for methylenes adjacent to unquaternized nitrogen has shifted to approximately 3.0 ppm. This is consistent with the desired quaternization of about 40% of the nitrogens.

#### EXAMPLE 7

##### Formation of amine oxide of (tetraethylenepentamine)<sub>5</sub>-(2-hydroxypropyl)<sub>4</sub> E<sub>7</sub>

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added (108 gm, 0.01 mole) of the polyamine comprising an average of 5 tetraethylene-pentamine blocks wherein each block is connected by a 2-hydroxypropyl unit (prepared as in Example 1) wherein each substitutable backbone site (27 -NH sites + 4 -OH sites) is ethoxylated to an average of 7 ethyleneoxy units per site, the ethoxylated material having an average molecular weight of 10,767. This material comprises an average 0.25 moles of oxidizable nitrogen atoms per mole of polymer. To this material is added hydrogen peroxide (50 g of a 30 wt % solution in water, 0.45 mol), the flask is stoppered and after an initial exotherm the solution is stirred at room temperature overnight. <sup>1</sup>H-NMR (D<sub>2</sub>O) spectrum obtained on a sample of the reaction mixture indicates complete conversion. The resonances ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the original position at ~2.5 ppm to ~3.5 ppm. To the reaction solution

is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The material as obtained is suitably stored as a 51.1% active solution in water.

#### EXAMPLE 8

##### Formation of amine oxide of quaternized (tetraethylenepentamine)<sub>5</sub>-(2-hydroxypropyl)<sub>4</sub> E<sub>7</sub>

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added (87.4 gm, 0.008 mole) of the polyamine comprising an average of 5 tetraethylene-pentamine blocks wherein each block is connected by a 2-hydroxypropyl unit (prepared as in Example 1) wherein each substitutable backbone site (27 -NH sites + 4 -OH sites) is ethoxylated to an average of 7 ethyleneoxy units per site, the ethoxylated material having an average molecular weight of 10,767, which is then further modified by quaternization to approximately 40% with dimethyl sulfate (as in Example 6) to an average molecular weight of approximately 10,927. To this material is added hydrogen peroxide (48 g of a 30 wt % solution in water, 0.42 mol), and water (~50 g). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. <sup>1</sup>H-NMR (D<sub>2</sub>O) spectrum obtained on a sample taken from the reaction mixture indicates complete conversion of the resonances attributed to the methylene peaks previously observed in the range of 2.5-3.0 ppm to a material having methylenes with a chemical shift of approximately 3.7 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The desired material with ~40% of the nitrogens quaternized and 60% of the nitrogens oxidized to amine oxide is obtained and is suitably stored as a 44.9% active solution in water.

#### EXAMPLES 9 & 10

The following describe high density liquid detergent compositions according to the present invention:

Ingredients	weight %	
	9	10
Polyhydroxy Coco-Fatty Acid Amide	3.65	3.50
C <sub>12</sub> -C <sub>13</sub> Alcohol Ethoxylate E <sub>9</sub>	3.65	0.80
Sodium C <sub>12</sub> -C <sub>15</sub> Alcohol Sulfate	6.03	2.50
Sodium C <sub>12</sub> -C <sub>15</sub> Alcohol Ethoxylate E <sub>2.5</sub> Sulfate	9.29	15.10

C <sub>10</sub> Amidopropyl Amine	0	1.30
Citric Acid	2.44	3.0
Fatty Acid (C <sub>12</sub> -C <sub>14</sub> )	4.23	2.00
Ethanol	3.00	2.81
Monoethanolamine	1.50	0.75
Propanediol	8.00	7.50
Boric Acid	3.50	3.50
Tetraethylenepentamine	0	1.18
Sodium Toluene Sulfonate	2.50	2.25
NaOH	2.08	2.43
Minors *	1.60	1.30
Soil Release Polymer**	0.50	0.50
Water	balance	balance

\* Minors - includes optical brightener and enzymes (protease, lipase, cellulase, and amylase).

\*\* Soil release polymer according to Example 5.

Compositions of the present invention are also prepared by preparing high density granular formulas according to this example utilizing the cotton soil release polymers alone or in combination with other soil release polymers.

#### EXAMPLES 11-14

<u>Ingredient</u>	<u>weight %</u>			
	11	12	13	14
Sodium C <sub>11</sub> -C <sub>13</sub> alkylbenzenesulfonate	13.3	13.7	10.4	11.1
Sodium C <sub>14</sub> -C <sub>15</sub> alcohol sulfate	3.9	4.	4.5	11.2
Sodium C <sub>14</sub> -C <sub>15</sub> alcohol ethoxylate (0.5) sulfate	2.0	2.0	0.0	0.0
Sodium C <sub>14</sub> -C <sub>15</sub> alcohol ethoxylate (6.5)	0.5	0.5	0.5	1.0
Tallow fatty acid	0.0	0.0	0.0	1.1
Sodium tripolyphosphate	0.0	41.0	0.0	0.0
Zeolite A, hydrate (0.1-10 micron size)	26.3	0.0	21.3	28.0
Sodium carbonate	23.9	12.4	25.2	16.1
Sodium Polyacrylate (45%)	3.4	0.0	2.7	3.4
Sodium silicate (1:6 ratio NaO/SiO <sub>2</sub> )(46%)	2.4	6.4	2.1	2.6
Sodium sulfate	10.5	10.9	8.2	15.0
Sodium perborate	1.0	1.0	5.0	0.0
Poly(ethyleneglycol), MW ~4000 (50%)	1.7	0.4	1.0	1.1

Citric acid	0.0	0.0	3.0	0.0
Nonyl ester of sodium p-hydroxybenzene-sulfonate	0.0	0.0	5.9	0.0
Non-cotton Soil release polymer*	0.0	0.0	0.5	0.5
Soil release polymer Example 6	0.5	0.5	0.5	0.5
Moisture	7.5	3.1	6.1	7.3

\* Non-cotton soil release polymer as taught in U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995, disclosed herein above.

Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, protease, lipase, cellulase, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including  $\text{CaCO}_3$ , talc, silicates, etc.

Aqueous crutcher mixes of heat and alkali stable components of the detergent compositions are prepared and spray-dried and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown. The soil release agents of the present invention can be, for example, pulverized and admixed in an amount sufficient for use at a level of 0.5% by weight in conjunction with the detergent compositions.

Cotton soil release agents of the present invention are especially useful in conventional laundry detergent compositions such as those typically found in granular detergents or laundry bars. U.S. Patent 3,178,370, Okenfuss, issued April 13, 1965, describes laundry detergent bars and processes for making them. Philippine Patent 13,778, Anderson, issued September 23, 1980, describes synthetic detergent laundry bars. Methods for making laundry detergent bars by various extrusion methods are well known in the art.

#### EXAMPLE 15

<u>Ingredients</u>	<u>Weight %</u>
C <sub>12</sub> linear alkyl benzene sulfonate	30
Phosphate (as sodium tripolyphosphate)	7
Sodium carbonate	25
Sodium pyrophosphate	7
Coconut monoethanolamide	2
Zeolite A, (0.1-10 micron)	5
Carboxycellulose	0.2
Ethylenediamine disuccinate chelant (EDDS)	0.4
Polyacrylate (MW = 1400)	0.2
Nonanolyoxybenzenesulfonate	5

Soil release agent*	0.5
Non-cotton soil release agent **	0.5
Sodium percarbonate ***	5
Brightener, perfume	0.2
Protease	0.3
Calcium sulfate	1
Magnesium sulfate	1
Water	4
Filler****	Balance to 100

\*Soil release polymer according to Example 7.

\*\*Non-cotton soil release agent according to U.S. Patent 4,968,451, J.J. Scheibel and E.P. Gosselink, issued November 6, 1990 and disclosed herein above.

\*\*\* Average particle size of 400 to 1200 microns.

\*\*\* Can be selected from convenient materials such as Calcium carbonate, talc, clay, silicates, and the like.

The detergent bars are processed in conventional soap or detergent bar making equipment as commonly used in the art. The soil release agent is pulverized and admixed in an amount sufficient for use at a level of 0.5% by weight in conjunction with the detergent compositions.

Compositions of the present invention are also prepared by preparing bar formulas according to Examples 16 and 17.

#### EXAMPLES 16 & 17

Laundry bars suitable for hand-washing soiled fabrics are prepared by standard extrusion processes and comprise the following:

<u>Ingredients</u>	<u>weight %</u>	
	<u>16</u>	<u>17</u>
LAS	12	6
Soap	44	29
Sodium tripolyphosphate	5	5
Sodium Carbonate	4	6
Optical brightener	0.03	0
Talc	0	35.5
Perfume	0.45	0
Sodium sulfate	0.29	0
Bentonite clay	12.81	0
Sodium chloride	2	2
Non-cotton soil release agent *	0.5	0.5

Soil release agent according to Example 7	0.5	
Soil release agent according to Example 8		0.5
Other**	0.42	1.5
Water	balance	balance

\* According to U.S. Patent 4,702,857, Gosselink, issued October 27, 1987 disclosed herein above.

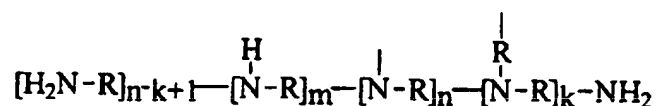
\*\* Can be selected from convenient materials such as Calcium carbonate, talc, clay, silicates, and the like.

## WHAT IS CLAIMED IS:

1. A water-soluble or dispersible, modified polyamine compound comprising a polyamine backbone corresponding to the formula:

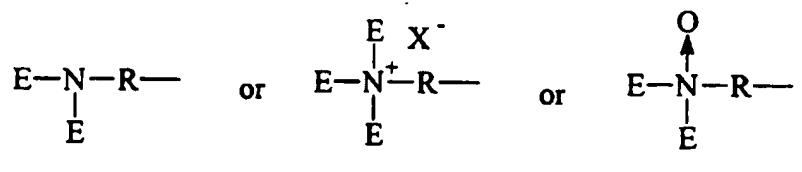


having a modified polyamine formula  $V_{(n+1)}W_mY_nZ$  or a polyamine backbone corresponding to the formula:

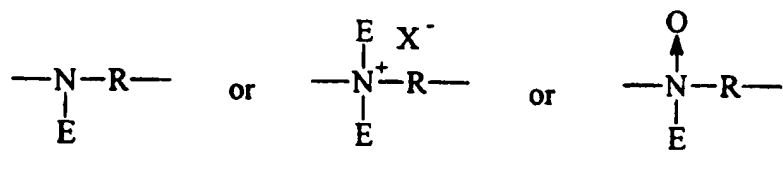


having a modified polyamine formula  $V_{(n-k+1)}W_mY_nY'_kZ$ , wherein  $k$  is less than or equal to  $n$ , said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

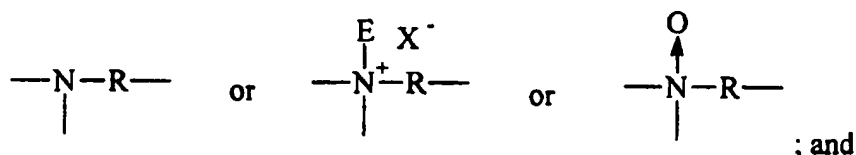
- i)  $V$  units are terminal units having the formula:



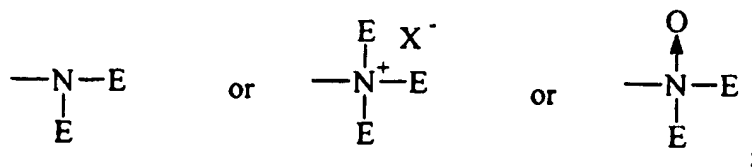
- ii)  $W$  units are backbone units having the formula:



- iii)  $Y$  units are branching units having the formula:



- iv)  $Z$  units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C<sub>2</sub>-C<sub>12</sub> alkylene, -(R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, (CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>- and mixtures thereof; provided that when R comprises C<sub>1</sub>-C<sub>12</sub> alkylene R also comprises at least one (R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, or -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-unit, preferably -(R<sup>1</sup>O)<sub>x</sub>R<sup>5</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OH)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)<sub>w</sub>-, -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-, and mixtures thereof; ; R<sup>1</sup> is C<sub>2</sub>-C<sub>6</sub> alkylene and mixtures thereof, preferably ethylene; R<sup>2</sup> is hydrogen, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof, preferably hydrogen; R<sup>3</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxy-alkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, -C(O)-, -C(O)NHR<sup>5</sup>NHC(O)-, -C(O)(R<sup>4</sup>)<sub>r</sub>C(O)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>OCH<sub>2</sub>CH-(OH)CH<sub>2</sub>-, and mixtures thereof, preferably C<sub>1</sub>-C<sub>6</sub> alkyl and mixtures thereof, more preferably methyl; R<sup>4</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>4</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, and mixtures thereof, preferably C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, and mixtures thereof, more preferably, ethylene, butylene, and mixtures thereof; R<sup>5</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene or C<sub>6</sub>-C<sub>12</sub> arylene, E units are selected from the group consisting of -(CH<sub>2</sub>)<sub>p</sub>-CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof, preferably -(R<sup>1</sup>O)<sub>x</sub>B; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, -(CH<sub>2</sub>)<sub>q</sub>-SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>CH(SO<sub>3</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-CH(SO<sub>2</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -PO<sub>3</sub>M, and mixtures thereof; preferably hydrogen; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; k has the value from 0 to 20; m has the value from 4 to 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

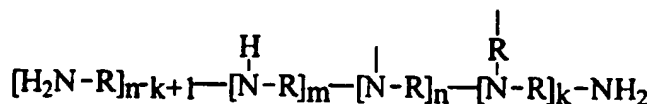


## 2. A laundry composition comprising:

- a) at least 0.001% by weight, a water-soluble or dispersible, bleach stable, modified polyamine cotton soil release agent comprising a polyamine backbone corresponding to the formula:

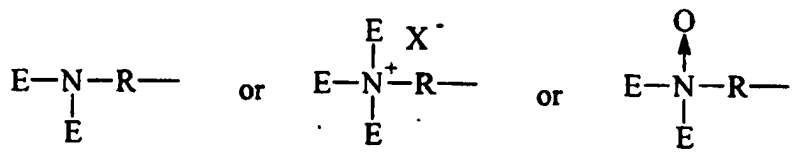


having a modified polyamine formula  $V_{(n+1)}W_mY_nZ$  or a polyamine backbone corresponding to the formula:

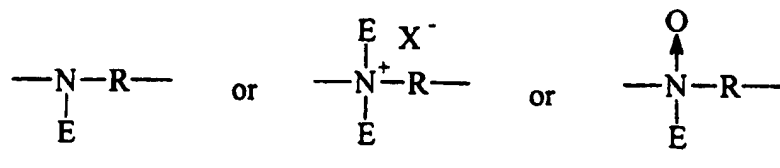


having a modified polyamine formula  $V_{(n-k+1)}W_mY_nY'_kZ$ , wherein  $k$  is less than or equal to  $n$ , said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

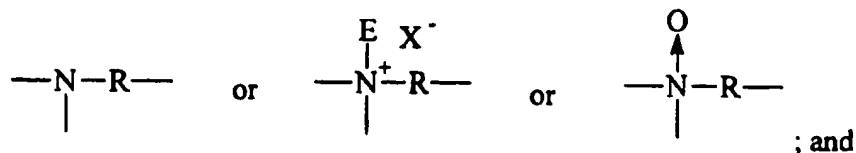
- i) V units are terminal units having the formula:



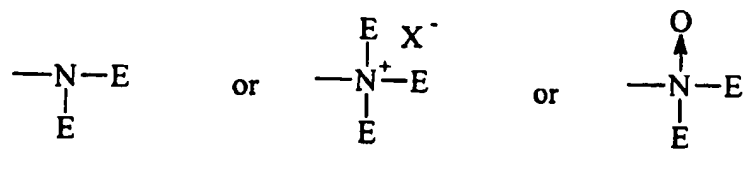
- ii) W units are backbone units having the formula:



- iii) Y units are branching units having the formula:



- iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C<sub>2</sub>-C<sub>12</sub> alkylene, -(R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, (CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>- and mixtures thereof; provided that when R comprises C<sub>1</sub>-C<sub>12</sub> alkylene R also comprises at least one (R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, or -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-unit, preferably -(R<sup>1</sup>O)<sub>x</sub>R<sup>5</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OH)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)<sub>w</sub>-, -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-, and mixtures thereof; ; R<sup>1</sup> is C<sub>2</sub>-C<sub>6</sub> alkylene and mixtures thereof, preferably ethylene; R<sup>2</sup> is hydrogen, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof, preferably hydrogen; R<sup>3</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxy-alkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, -C(O)-, -C(O)NHR<sup>5</sup>NHC(O)-, -C(O)(R<sup>4</sup>)<sub>r</sub>C(O)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>OCH<sub>2</sub>CH-(OH)CH<sub>2</sub>-, and mixtures thereof, preferably C<sub>1</sub>-C<sub>6</sub> alkyl and mixtures thereof, more preferably methyl; R<sup>4</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>4</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, and mixtures thereof, preferably C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, and mixtures thereof, more preferably, ethylene, butylene, and mixtures thereof; R<sup>5</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene or C<sub>6</sub>-C<sub>12</sub> arylene, E units are selected from the group consisting of -(CH<sub>2</sub>)<sub>p</sub>-CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof, preferably -(R<sup>1</sup>O)<sub>x</sub>B; B is hydrogen, -(CH<sub>2</sub>)<sub>q</sub>-SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>CH(SO<sub>3</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-CH(SO<sub>2</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -PO<sub>3</sub>M, and mixtures thereof; preferably hydrogen; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; k has the value from 0 to 20; m has the value from 4 to about 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and

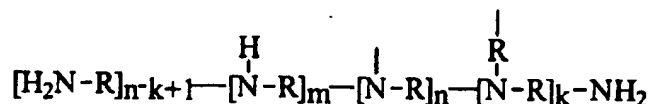
b) the balance carriers and adjunct material said adjunct materials selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach activators, soil release polymers, dye transfer agents, dispersants, enzymes, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, and mixtures thereof.

3. A laundry detergent composition comprising:

- a) at least 0.01% to 95% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, and ampholytic surfactants, and mixtures thereof;
- b) from 0.01 to 10% by weight, a water-soluble or dispersible, bleach stable, modified polyamine cotton soil release agent comprising a polyamine backbone corresponding to the formula:

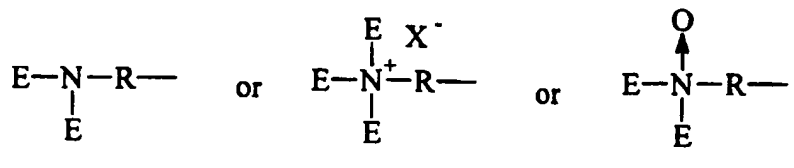


having a modified polyamine formula  $V_{(n+1)}W_mY_nZ$  or a polyamine backbone corresponding to the formula:

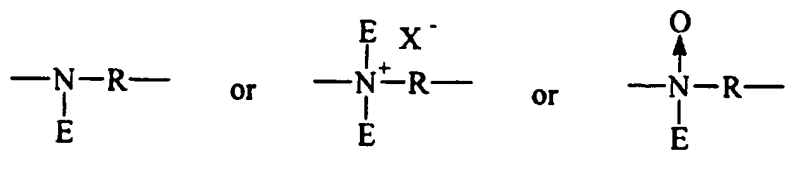


having a modified polyamine formula  $V_{(n-k+1)}W_mY_nY'_kZ$ , wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

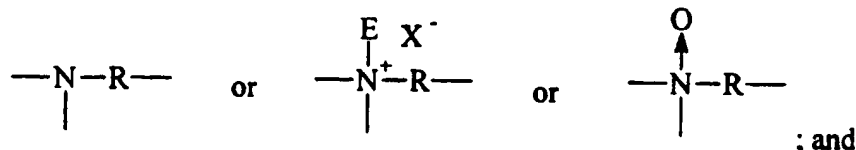
- i) V units are terminal units having the formula:



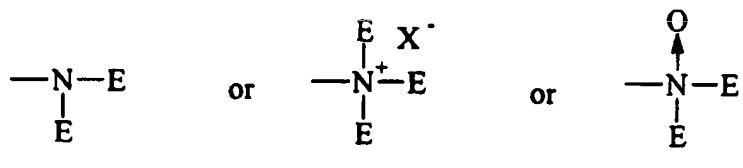
- ii) W units are backbone units having the formula:



iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



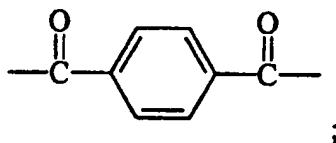
wherein backbone linking R units are selected from the group consisting of C<sub>2</sub>-C<sub>12</sub> alkylene, -(R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, (CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>- and mixtures thereof; provided that when R comprises C<sub>1</sub>-C<sub>12</sub> alkylene R also comprises at least one (R<sup>1</sup>O)<sub>x</sub>R<sup>3</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>)<sub>w</sub>-, or -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-unit, preferably - (R<sup>1</sup>O)<sub>x</sub>R<sup>5</sup>(OR<sup>1</sup>)<sub>x</sub>-, -(CH<sub>2</sub>CH(OH)CH<sub>2</sub>O)<sub>z</sub>(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)<sub>w</sub>-, -CH<sub>2</sub>CH(OR<sup>2</sup>)CH<sub>2</sub>-, and mixtures thereof; ; R<sup>1</sup> is C<sub>2</sub>-C<sub>6</sub> alkylene and mixtures thereof, preferably ethylene; R<sup>2</sup> is hydrogen, - (R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof, preferably hydrogen; R<sup>3</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxy-alkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, -C(O)-, -C(O)NHR<sup>5</sup>NHC(O)-, -C(O)(R<sup>4</sup>)<sub>t</sub>C(O)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O(R<sup>1</sup>O)<sub>y</sub>R<sup>1</sup>OCH<sub>2</sub>CH(OH)CH<sub>2</sub>-, and mixtures thereof, preferably C<sub>1</sub>-C<sub>6</sub> alkyl and mixtures thereof, more preferably methyl; R<sup>4</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>4</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, and mixtures thereof, preferably C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>8</sub>-C<sub>12</sub> arylalkylene, and mixtures thereof, more preferably, ethylene, butylene, and mixtures thereof; R<sup>5</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene or C<sub>6</sub>-C<sub>12</sub> arylene, E units are selected from the group consisting of -(CH<sub>2</sub>)<sub>p</sub>-

CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -(R<sup>1</sup>O)<sub>x</sub>B, and mixtures thereof, preferably -(R<sup>1</sup>O)<sub>x</sub>B; B is hydrogen, -(CH<sub>2</sub>)<sub>q</sub>-SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>CH(SO<sub>3</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-CH(SO<sub>2</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -PO<sub>3</sub>M, and mixtures thereof; preferably hydrogen; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; k has the value from 0 to 20; m has the value from 4 to 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1;

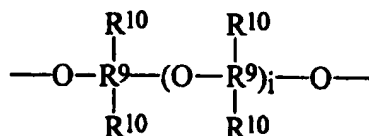
- c) form 0.01 to 95% adjunct ingredients selected from the group consisting of builders, optical brighteners, bleaches, soil release polymers, bleach boosters, bleach activators, dye transfer agents, dispersants, protease enzymes, lipase enzymes, cellulase enzymes, oxidase enzymes, amylase enzymes, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, and mixtures thereof; and
- d) the balance carriers.

4. A composition according to any of Claims 1-3 further comprising a non-cotton soil release polymer comprising:

- a) a backbone comprising:
  - i) at least one moiety having the formula:



- ii) at least one moiety having the formula:



wherein R<sup>9</sup> is C<sub>2</sub>-C<sub>6</sub> linear alkylene, C<sub>3</sub>-C<sub>6</sub> branched alkylene, C<sub>5</sub>-C<sub>7</sub> cyclic alkylene, and mixtures thereof; R<sup>10</sup> is independently selected from hydrogen or -L-SO<sub>3</sub><sup>-</sup>M<sup>+</sup>; wherein L is a side chain moiety selected from the group consisting of alkylene,

oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxy-alkyleneoxyarylene, poly(oxyalkylene)oxyarylene, alkylene-poly(oxyalkylene), and mixtures thereof; M is hydrogen or a salt forming cation; i has the value of 0 or 1;

- iii) at least one trifunctional, ester-forming, branching moiety;
- iv) at least one 1,2-oxyalkyleneoxy moiety; and
- b) one or more capping units comprising:
  - i) ethoxylated or propoxylated hydroxyethanesulfonate or ethoxylated or propoxylated hydroxypropanesulfonate units of the formula  $(\text{MO}_3\text{S})(\text{CH}_2)_m(\text{R}^{11}\text{O})_n^-$ , where M is a salt forming cation,  $\text{R}^{11}$  is ethylene, propylene, and mixtures thereof, m is 0 or 1, and n is from 1 to 20;
  - ii) sulfoaroyl units of the formula  $-(\text{O})\text{C}(\text{C}_6\text{H}_4)(\text{SO}_3^-\text{M}^+)$ , wherein M is a salt forming cation;
  - iii) modified poly(oxyethylene)oxy monoalkyl ether units of the formula  $\text{R}^{12}\text{O}(\text{CH}_2\text{CH}_2\text{O})_k^-$ , wherein  $\text{R}^{12}$  contains from 1 to 4 carbon atoms and k is from 3 to 100; and
  - iv) ethoxylated or propoxylated phenolsulfonate end-capping units of the formula  $\text{MO}_3\text{S}(\text{C}_6\text{H}_4)(\text{OR}^{13})_n\text{O}^-$ , wherein n is from 1 to 20; M is a salt-forming cation; and  $\text{R}^{13}$  is ethylene, propylene, and mixtures thereof.

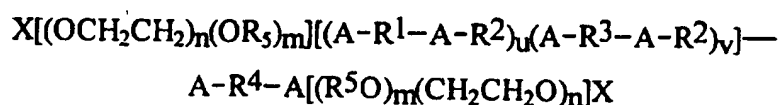
5. A composition according to any of Claims 1-3 further comprising a non-cotton soil release agent comprises a sulfonated oligomeric ester composition comprising the sulfonated product of a pre-formed, substantially linear ester oligomer, said linear ester oligomer comprising, per mole,
  - a) 2 moles of terminal units wherein from about 1 mole to about 2 moles of said terminal units are derived from an olefinically unsaturated component selected from the group consisting of allyl alcohol and methallyl alcohol, and any remaining of said terminal units are other units of said linear ester oligomer;
  - b) from 1 mole to 4 moles of nonionic hydrophile units, said hydrophile units being derived from alkyleneoxides, said alkylene oxides comprising from 50% to 100% ethylene oxide;

- c) from 1.1 moles to 20 moles of repeat units derived from an aryldicarbonyl component wherein said aryldicarbonyl component is comprised of from 50% to 100% dimethylterephthalate, whereby the repeat units derived from said dimethylterephthalate are terephthaloyl; and
- d) from 0.1 moles to 19 moles of repeat units derived from a diol component selected from the group consisting of C<sub>2</sub>-C<sub>4</sub> glycols;

wherein the extent of sulfonation of said sulfonated oligomeric ester composition is such that said terminal units are chemically modified by

- e) from 1 mole to 4 moles of terminal unit substituent groups of formula -SO<sub>x</sub>M wherein x is 2 or 3, said terminal unit substituent groups being derived from a bisulfite component selected from the group consisting of HSO<sub>3</sub>M wherein M is a conventional water-soluble cation.

6. A composition according to any of Claims 1-3 further comprising a non-cotton soil release agent comprising compounds of the formula



wherein each of the A moieties is selected from the group consisting of



and combinations thereof, each of the R<sup>1</sup> moieties is selected from the group consisting of 1,4-phenylene and combinations thereof with 1,3-phenylene, 1,2-phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2'-biphenylene, 4,4'-biphenylene, C<sub>1</sub>-C<sub>8</sub> alkylene, C<sub>1</sub>-C<sub>8</sub> alkenylene and mixtures thereof the R<sup>2</sup> moieties are each selected from the group consisting of ethylene moieties, substituted ethylene moieties having C<sub>1</sub>-C<sub>4</sub> alkyl, alkoxy substituents, and mixtures thereof; the R<sup>3</sup> moieties are substituted C<sub>2</sub>-C<sub>18</sub> hydrocarbylene moieties having at least one -CO<sub>2</sub>M, -O[(R<sup>5</sup>O)<sub>m</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>]<sub>w</sub>X or -A[(R<sup>2</sup>-A-R<sup>4</sup>-A)]<sub>w</sub>[(R<sup>5</sup>O)<sub>m</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>]<sub>w</sub>X substituent; the R<sup>4</sup> moieties are R<sup>1</sup> or R<sup>3</sup> moieties, or mixtures thereof; each R<sup>5</sup> is C<sub>1</sub>-C<sub>4</sub> alkylene, or the moiety -R<sup>2</sup>-A-R<sup>6</sup>- wherein R<sup>6</sup> is a C<sub>1</sub>-C<sub>12</sub> alkylene, alkenylene, arylene, or alkarylene moiety; each M is hydrogen or a water-soluble cation; each X is C<sub>1</sub>-C<sub>4</sub> alkyl; the indices m and n have the values such that the moiety -(CH<sub>2</sub>CH<sub>2</sub>O)- comprises at least 50% by weight of the moiety [(R<sup>5</sup>O)<sub>m</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>],

provided that when  $R^5$  is the moiety  $-R^2-A-R^6-$ ,  $m$  is 1; each  $n$  is at least about 10; the indices  $u$  and  $v$  have the value such that the sum of  $u + v$  is from about 3 to 25; the index  $w$  is 0 or at least 1; and when  $w$  is at least 1  $u$ ,  $v$  and  $w$  have the value such that the sum of  $u + v + w$  is from 3 to 25.

7. A composition according to any of Claims 1-3 further comprising a non-cotton soil release agent comprising:

- A) at least 10% by weight of a substantially linear sulfonated poly-ethoxy/propoxy end-capped ester having molecular weight ranging from 500 to 8,000; said ester consisting essentially of on a molar basis:
- i) from 1 to 2 moles of sulfonated poly ethoxy/propoxy end-capping units of the formula:



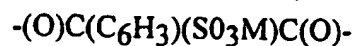
wherein  $M$  is a salt-forming cation such as sodium or of tetraalkylammonium,  $m$  is 0 or 1,  $R$  is ethylene, propylene, and mixtures thereof; and  $n$  is from 0 to 2; and mixtures thereof;

- ii) from 0.5 to 66 moles of units selected from the group consisting of:
- a) oxyethyleneoxy units;
- b) a mixture of oxyethyleneoxy and oxy-1,2,-propyleneoxy units wherein said oxyethyleneoxy units are present in an oxyethyleneoxy of oxy-1,2-propyleneoxy mole ratio ranging from 0.5:1 to 10:1; and
- c) a mixture of a) or b) with poly(oxyethylene)oxy units have a degree of polymerization of from 2 to 4; provided that when said poly(oxyethylene)oxy units have a degree of polymerization of 2, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.33:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 3; the mole ration of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.22:1; and when said poly(oxyethylene)oxy units have a degree of polymerization equal to 4, the mole ratio of



poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.14:1;

- iii) from 1.5 to 40 moles of terephthaloyl units; and
- iv) from 0 to 26 moles of 5-sulphophthaloyl units of the formula:



wherein M is a salt forming cation; and

- B) from 0.5% to 20% by weight of ester, of one or more crystallization-reducing stabilizers.

- 8. A composition according to any of Claims 1-7 further comprising greater than 0.5% carboxy methyl cellulose.

# INTERNATIONAL SEARCH REPORT

Intern: al Application No. PCT/US 97/06917

## A. CLASSIFICATION OF SUBJECT MATTER

C 11 D 3/37, C 08 G 73/02

According to International Patent Classification (IPC) or to both national classification and IPC <sup>6</sup>

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 11 D, C 08 G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 2 184 739 (SANDOZ) 01 July 1987 (01.07.87), claims 1-2.	1
A	--	2-7
A	EP, A, 0 233 010 (THE PROCTER & GAMBLE) 19 August 1987 (19.08.87), page 4, line 52 - page 8, line 29.	1-8
A	--	
A	US, A, 4 891 160 (VANDER MEER) 02 January 1990 (02.01.90), column 5, lines 37-45; claim 1 (cited in the application).	1-8
	--	

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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Date of the actual completion of the international search  
07 August 1997

Date of mailing of the international search report

19. 09. 97

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

-2-

International Application No

PCT/US 97/06917

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A, 95/32 272 (THE PROCTER & GAMBLE) 30 November 1995 (30.11.95), claims 1-6 (cited in the application). -----	1-8

## ANHANG

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

## ANNEX

to the International Search  
Report to the International Patent  
Application No.

## ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 97/06917 SAE 160355

In diesem Anhang sind die Mitglieder  
der Patentfamilien der in obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
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membres de la famille de brevets  
relatifs aux documents de brevets cités  
dans le rapport de recherche inter-  
national visé ci-dessus. Les renseigne-  
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Im Recherchenbericht angeführtes Patentdokument Patent document cited In search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
GB A1 2184739	01-07-87	CH A3 674786 CH B 674786 FR A1 2557602 FR B1 2557602 GB A1 2154615 GB B2 2154615 GB B2 2184739 IT A 1199927 JP A2 60185791 US A 4599087 DE A1 3446282 DE C2 3446282 IT A0 8847507 GB A0 8500032 GB A0 8702135	31-07-90 31-01-91 05-07-85 12-06-87 11-09-85 09-12-87 09-12-87 05-01-89 15-08-85 08-07-86 11-07-85 07-07-88 03-01-85 13-02-85 04-03-87
EP A2 233010	19-06-87	US A 4689167 AU A1 68149787 AU A1 61933790 AU B2 631241 CA A1 1293420 CN A 87101761 CN B 1008634 DK A0 475787 DK A 475787 EP A3 233010 FI A0 870419 FI A 870419 FI B 83431 FI C 83431 GB A1 2186589 GB B2 2186589 HK A 2529793 JP A2 62253694 JP B4 7116473 KR B1 9504822 PL A 23085 SG A 328793 AT E 62505 AU A1 68150787 AU B2 681608 CA A1 1293419 CN A 87101893 CN B 1008635 DE C0 3769161 DK A0 474787 DK A 474787 DK A 306794 EP A2 2332114 EP A2 2332114 EP A2 672296 EP A3 3467296 EP B1 2332114 FI A0 8704220 FI A 8704220 GB A0 8701819 GB A0 8701834 GB A1 23185981 GB B2 23185981 GR T3 30001754 HK A 181793 JP A2 62253693 KR B1 9504821 PL A 230997 SG A 1209792 US A 4663071 US B1 4663071 CA A1 1223441 CA A1 1223441 CA A0 3047246	25-08-87 06-08-87 27-11-90 19-11-92 24-12-91 16-09-87 04-07-90 29-01-87 31-07-87 02-12-87 30-01-87 31-07-87 28-03-91 10-07-91 19-08-87 26-09-90 11-06-93 05-11-87 13-12-95 13-05-95 10-04-89 21-05-93 15-04-91 06-08-87 23-02-89 24-12-91 16-09-87 04-07-90 16-05-91 29-01-87 31-07-87 16-03-94 13-08-87 02-12-87 09-05-90 09-01-91 10-04-91 30-01-87 31-07-87 04-03-87 04-03-87 05-08-87 14-03-90 23-11-92 13-03-93 05-11-87 13-05-95 10-04-89 29-01-93 05-05-87 07-04-92 13-12-95 09-05-89 17-01-91

EP	A2	192442	27-08-86
EP	A3	192441	09-12-87
EP	A3	192442	09-12-87
EP	B1	192442	05-12-90
JP	A2	61246298	01-11-86
US	A	4687592	18-08-87

US	A	4891160	02-01-90	keine - none - rien
WD	A1	9532272	30-11-95	
	AU	A1	23870/95	18-12-95
	CA	AA	2189749	30-11-95
	EP	A1	760846	12-03-97
	US	A	5565145	15-10-96

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